Controlled Assembly Based on Multibridging Thiolate Ligands: New Polymeric Silver(I) Complexes with One-Dimensional Chain and Three-Dimensional Network Structures

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Introduction

The research in the design of infinite molecular components with specific chains and networks, or so-called crystal engineering, has become an area of current interest over recent years.[1] Much work has focused on the use of polypyridyl or pyrazines to act as exo-bidentate ligands to linearly bridge metal ions, generating oligomeric and polymeric metal complexes with infinite chain structures and two- or three-dimensional networks.[2−4] However, the design of inorganic chains and networks, especially the polymeric metal complexes with three-dimensional nets, is not well-developed.[5−8] Dithiolates acting as μ_2 or μ_3 bridging ligands were used to link metal ions such as Cu(I) or Ag(I) yielding the complexes with infinite chain structures.[5,6,8] Simple monothiolate ligands acting as μ_2 or μ_3 bridges are very common in transition metal chemistry,[9] however, those acting as μ_4 bridges linking four metal centers to form polymeric complexes in infinite chain or in network structures were not reported until recently.[10] We have explored ways to synthesize polymeric complexes with chain structure by using coinage metal ions and dithiolate ligands.[11] By changing from dithiolate to monothiolate ligands, we obtained a series of polymeric silver complexes.[12] Herein we report the syntheses and structures of two new silver complexes, $[\mathrm{Ag_6(\mu_3\text{-}SC_5H_4N)_4(\mu_4\text{-}SC_5H_4N)_2}]_n$ (**1**) with one-dimensional chain structure and $[\mathrm{Ag(\mu_2\text{-}SC_5H_4NH)Cl}]_n$ (**2**) with three-dimensional network structure ($\mathrm{SC_5H_4N}$ = pyridine-2-thionate ($^-$SPy), $\mathrm{SC_5H_4NH}$ = 1*H*-pyridine-2-thione (SPyH)). We find that it is possible to use this simple monothiolate ligands to generate unusual one-dimensional chain or three-dimensional network silver coordination polymers.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
semiempirical formula	$\mathrm{C_{30}H_{24}N_6Ag_6S_2}$	$\mathrm{C_5H_5NAgSCl}$
fw	1308.2	254.5
space group	$P2_1/c$	Cc
a (Å)	7.819(1)	11.055(16)
b (Å)	10.534(1)	11.250(16)
c (Å)	21.197(2)	7.452(7)
β (deg)	90.079(3)	130.12(6)
V (Å^3)	1746.1(4)	708.8(9)
Z	2	4
ρ_{calcd} (g cm^{-3})	2.429	2.385
T (°C)	23	23
μ (mm^{-1})	3.692	3.415
λ (Å, Mo Kα)	0.710 73	0.710 73
$R(F_o)^a$	0.071	0.027
$R_w(F_o)^b$	0.084	0.032

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Experimental Section

Synthesis of $[\mathrm{Ag_6(\mu_3\text{-}SC_5H_4N)_4(\mu_4\text{-}SC_5H_4N)_2}]_n$ (1). AgCl (0.14 g, 1 mmol) was added to SPyH (0.22 g, 2 mmol) in 20 mL of DMSO; after stirring for 0.5 h, AgCl was dissolved and 0.5 mL of triethylamine was added to the reaction mixture. Colorless block crystals of **1** were obtained by allowing the reaction mixture to stand in air for 1 day. IR (KBr, cm^{-1}): 445.4 (w), 486.0 (m), 632.5 (w), 719.3 (s), 757.9 (s). Anal. Calcd for $\mathrm{C_{30}H_{24}N_6Ag_6S_6}$: C, 27.55, 1.85, 6.42. Found: C, 27.25, 1.79, 6.20.

Synthesis of $[\mathrm{Ag(\mu_2\text{-}SC_5H_4NH)Cl}]_n$ (2). AgCl (0.14 g, 1 mmol) was added to SPyH (0.22 g, 2 mmol) in 20 mL $\mathrm{CH_3CN}$; after stirring for 0.5 h, AgCl was dissolved and a great amount of white precipitate was formed. The precipitate was collected and dissolved in 10 mL of DMSO. Light-yellow block crystals of **2** were obtained after allowing $\mathrm{Et_2O}$ vapor to diffuse into the DMSO solution for 5 days. IR (KBr, cm^{-1}): 443.6 (m), 489.8 (m), 621.0 (w), 723.2 (s), 756.0 (s). Anal. Calcd for $\mathrm{C_5H_5NAgSCl}$: C, 23.60, H, 1.98, N, 5.50. Found: C, 23.36, 1.89, 5.32.

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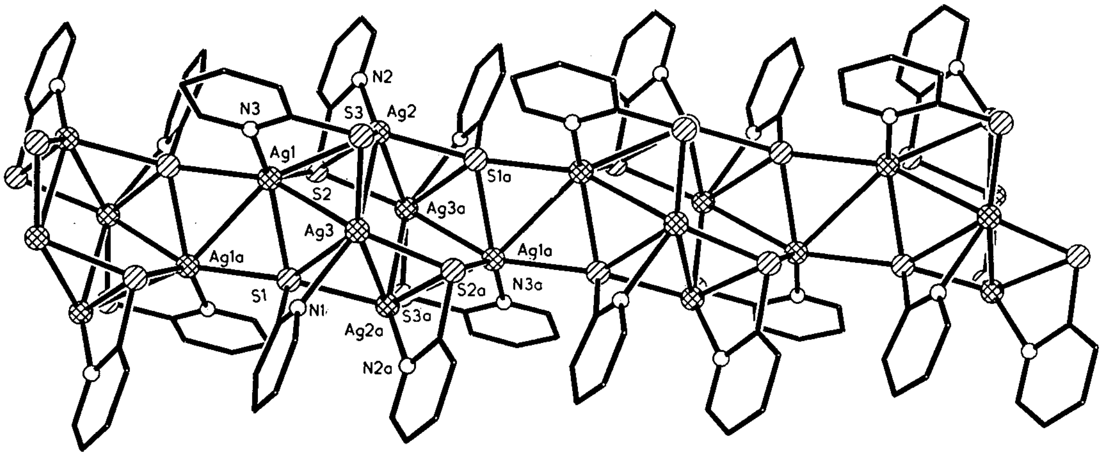


Figure 1. View of the one-dimensional chains, running along the *a* axis in [Ag$_6$(μ_3-SC$_5$H$_4$N)$_4$(μ_4-SC$_5$H$_4$N)$_2$]$_n$ with the ellipsoids drawn at the 30% probability level. Only silver, chlorine, and sulfur atoms are labeled.

Table 2. Selected Bond Distances and Angles for **1** and **2**

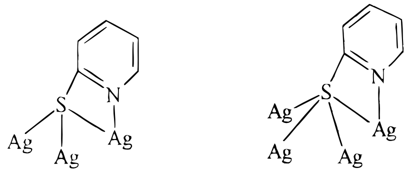
Data for **1**			
Ag(1)−Ag(2)	2.959 (2)	Ag(2)−S(1)	2.642 (5)
Ag(1)−Ag(3)	3.051 (2)	Ag(2)−S(2)	2.959 (5)
Ag(2)−Ag(3)	3.071 (2)	Ag(2)−S(3)	2.460 (5)
Ag(2)−Ag(3a)	3.279 (2)	Ag(2)−N(2)	2.371 (16)
Ag(3)−Ag(2a)	3.279 (2)	Ag(3)−S(3)	2.456 (5)
Ag(1)−S(1)	2.786 (5)	Ag(3)−S(1a)	2.912 (5)
Ag(1)−S(2)	2.607 (5)	Ag(3)−S(2a)	2.576 (5)
Ag(1)−N(3)	2.277 (15)	Ag(3)−N(1a)	2.454 (16)
Ag(1)−S(1a)	2.675 (5)		
Ag(2)−Ag(1)−Ag(3)	61.4(1)	S(1)−Ag(2)−N(2)	100.8(4)
Ag(1)−Ag(2)−Ag(3)	60.8(1)	S(2)−Ag(2)−N(2)	59.2(4)
Ag(1)−Ag(2)−Ag(3a)	89.1(1)	S(3)−Ag(2)−N(2)	139.8(4)
Ag(3)−Ag(2)−Ag(3a)	88.2(1)	S(3)−Ag(3)−S(2a)	111.3(2)
Ag(1)−Ag(3)−Ag(2)	57.8(1)	S(3)−Ag(3)−N(1a)	134.0(4)
Ag(1)−Ag(3)−Ag(2a)	91.0(1)	S(2A)−Ag(3)−N(1a)	104.7(4)
Ag(2)−Ag(3)−Ag(2a)	91.8(1)	Ag(2)−S(1)−Ag(1a)	147.5(2)
S(2)−Ag(1)−N(3)	141.0(4)	Ag(2)−S(1)−Ag(3a)	72.2(1)
S(2)−Ag(1)−S(1a)	95.2(2)	Ag(1A)−S(1)−Ag(3a)	136.7(2)
N(3)−Ag(1)−S(1a)	93.3(4)	Ag(1)−S(2)−Ag(2)	63.9(1)
S(1)−Ag(2)−S(2)	105.3(2)	Ag(1)−S(2)−Ag(3a)	115.5(2)
S(1)−Ag(2)−S(3)	110.2(2)	Ag(2)−S(2)−Ag(3a)	72.3(1)
S(2)−Ag(2)−S(3)	130.6(1)	Ag(2)−S(3)−Ag(3)	77.3(1)
Data for **2**			
Ag−Cl	2.626 (4)	Ag−S(a)	2.502 (4)
Ag−S	2.587 (4)	S−C(1)	1.745 (7)
Ag−Cl(a)	2.670 (5)		
Cl−Ag−S	101.1(1)	S−Ag−S(a)	121.5(1)
Cl−Ag−Cl(a)	95.2(1)	Cl(a)−Ag−S(a)	106.9(1)
S−Ag−Cl(a)	107.7(1)	Ag−Cl−Ag(a)	141.8(1)
Cl−Ag−S(a)	120.9(1)	Ag−S−Ag(b)	141.7(1)

The polymeric complexes can also be prepared from slowly mixing a ligand solution and a metal ion solution in an H type tube by controlling interface, similar to our former reports.[12]

X-ray Structural Characterization. Single crystals for **1** and **2** were mounted on glass fibers. Cell constants and data collections were performed on a Siemens Smart CCD diffractometer with graphite monochromitized Mo Kα radiation at 23 °C. Intensity data were obtained in the range $3 < 2\theta < 50°$ by using an ω scan technique. The data reductions were performed on a silicon graphics computer station with Smart CCD software. Crystallographic data are listed in Table 1.

For the structural analyses, all calculations were performed on an HP/586 computer with SHELXL-PC program.[13] The structures were refined through the use of the SHELXL-93 program.[14] The positions of the heavy atoms were determined by direct methods, and successive difference electron density maps located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropiclly. The positions of all hydrogen atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement. For **1**, the final refinement based on F_o for 2606 observations ($F \geq 2.0\sigma(F)$) and 217 variables led to convergence. For **2**, the final anisotropic refinement of all non-hydrogen atoms on F_o for 1101 observations ($F \geq 4.0\sigma(F)$) and 221 variables led to convergence. Table 2 gives the significant bond lengths and angles for **1** and **2**.

Chart 1. Coordination Modes of Mercaptopyridine Ligand



a b

Results and Discussion

Complex **1** is a polymer and the neutral hexanuclear [Ag$_6$(SPy)$_6$] constitutes the building-block unit. The hexanuclear unit possesses a crystallographic inversion center, and the structure is quite different from those of [{Ag(SR)}$_6$][15] (R = 3-(*tert*-butyldimethylsilyl)pyridine-2-thione) and [Cu$_6$(SPy)$_6$][16] with distorted octahedral M$_6$ cores. The units are linked by Ag−S bonds and Ag−Ag interactions to form a one-dimensional chain structure along the *a* axis in the crystal (Figure 1). The coordination environment of each silver atom is a distorted tetrahedron of S$_3$N, generated by the sulfur and nitrogen atoms of mercaptopyridine ligands. There are two kinds of coordination modes of mercaptopyridine ligands: the sulfur atom acts as a μ_3-bridge (S(2), S(3), S(2a), and S(3a)) linking three metal centers (Chart 1a) or as μ_4-bridge(S(1) and S(1a)) linking four metal centers (Chart 1b).

To our knowledge, the reports on μ_4-S bridges of thiolate ligands in transition metal compounds are very few,[10] and **1** is the first compound in which mercaptopyridine demonstrates not

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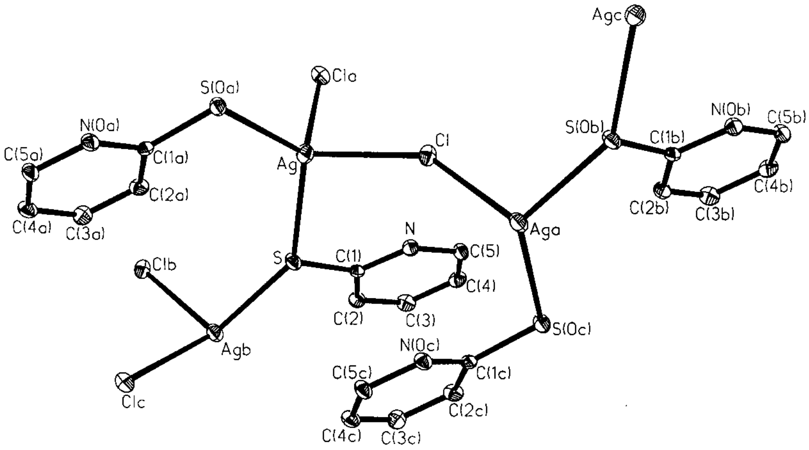


Figure 2. Local coordination around the silver atoms in $[Ag(\mu_2\text{-}SC_5H_4NH)Cl]_n$ with the ellipsoids drawn at the 30% probability level.

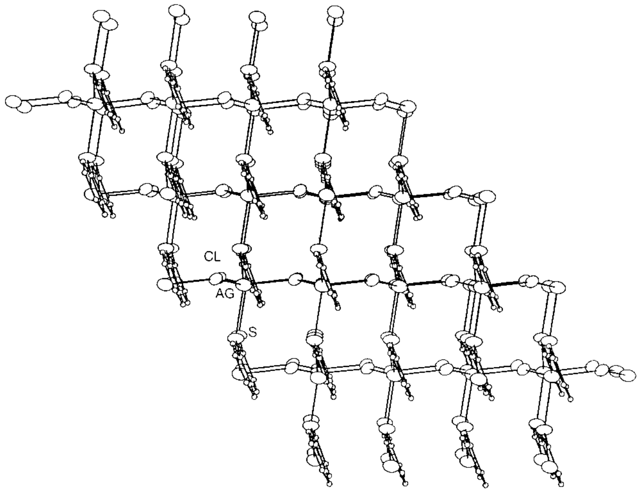
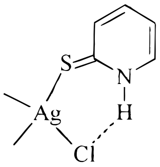


Figure 3. View of the three-dimensional network of $[Ag(\mu_2\text{-}SC_5H_4NH)Cl]_n$ along the *a* axis with the ellipsoids drawn at 30% probability level. Only silver, chlorine, and sulfur atoms are labeled.

only μ_4-S bridge but also a chelating ligand. The Ag−Ag separations range from 2.959(2) to 3.369(3) Å, indicating the existence of weak metal−metal interactions. The average bond distance of Ag−N (2.367(5) Å) is shorter than that of Ag−S (2.655(4) Å).

For **2**, the molecule exhibits three-dimensional network structure and the neutral mononuclear [Ag(SPyH)Cl] is the basic building-block unit. Figure 2 shows the local coordination around the silver atoms in the complex. Each silver atom is tetracoordinated in a distorted tetrahedral fashion of S_2Cl_2, generated by the sulfur atoms of two different SPyH molecules and two chloride atoms. Every two AgS_2Cl_2 tetrahedra share one vertex (S or Cl), thus, either chloride or sulfur atom in the complex is μ_2-bridge linking two metal centers to form the final network structure. All the pyridine rings are aligned so that their planes are nearly parallel to the *a* axis (average separation is ca. 6.86 Å). If one views along the *a* axis, the silver atoms bind SPyH and Cl to give apparently tetragonal channels with pores open (5.0 × 5.0 Å) in the crystal (Figure 3). The average Ag−Ag separations is 5.0 Å, preclusive of any direct metal−metal interaction. The average bond distance of Ag−Cl (2.648(5) Å) is longer than that of Ag−S (2.550(4) Å). The average value (109.9(1) Å) of Cl−Ag−S bond angles is much larger than that of Cl−Ag−Cl (95.2(1) Å) but is much smaller than that of S−Ag−S (121.5(1) Å). The Ag−Cl−Ag angle 141.8(1) Å is nearly the same as that of Ag−S−Ag (141.7(1) Å). An efficient intramolecuar hydrogen bond of N−H···Cl occurs in each building-block unit of [AgSPyHCl] in crystal (Chart 2), and the average N···Cl distance is 3.10 Å.

Chart 2. Intramolecular Hydrogen Bond in [AgSPyHCl]



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Supporting Information Available: Additional crystallographic details, complete listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atom positions (5 pages) for the complex **1** and **2** are available. Ordering information is given on any current masthead page.

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